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ANELASTIC MEASUREMENT OF DIFFUSION IN α-AgCd ALLOYS

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ABSTRACT. Measurements of the internal friction peak are made for three α-AgCd alloys with 24.3, 29.3 and 33.8 atomic percent Cd and 30.8% Zn α-brass. The peaks are due to changes in local order with the external stress. The activation energy corresponding to the relaxation process is found to be 39.36, 38.77 and 38.45 K cal/mole for the 24.3, 29.3 and 33.8 at. % Cd alloys respectively. For the grain boundary relaxation effects the activation energy is 39.7 K cal/mole for the 29.3% Cd alloy. The corresponding activation energies for the 30.8% brass are 39.17 and 39.84 K cal/mole.

The measured values of the relaxation time τ are used to calculate the diffusion coefficient of the Ag-Cd alloys. The calculated values are in good agreement with the directly measured diffusion coefficients of alloys of corresponding compositions.

INTRODUCTION

The measurements of anelastic effects caused by stress induced ordering and observed as an internal friction peak in some substitutional alloys present a method of obtaining diffusion coefficient at lower temperatures and in a time of the order of that required by a single atomic jump. The method has been applied extensively to study the diffusion in α-AgZn (Nowick, 1952) and α-CuZn (Leclaire, 1951) alloys and to a lesser extent in some other alloys. Both these authors have pointed out the advantages which may be gained by using this method to study small scale atomic movements in cases where conventional diffusion techniques are inapplicable on account of the long times and high temperature required. The principle of the method is briefly as follows : The application of stress to a random solid solution will, in general change the equilibrium configuration to a non-random one. Atomic redistribution must, therefore, follow the application of stress; this redistribution is accompanied by typical anelastic effects, such as, an internal friction peak and an elastic after effect.

This internal friction effect in substitutional solid solutions, first seen by Zener (1943) in 30% α-brass, has been observed later in many other substitutional alloys. These studies revealed that the magnitude of the effect goes up roughly

as the square of the solute concentration, and the process is an activated one with an activation energy close to that for diffusion in the alloys. On this evidence Zener (1947) interpreted the above effect as being due to a preferential orientation, under applied stress, of the axis of pairs of adjacent solute atoms into a particular crystallographic direction such that the axial strain set up by each pair in the lattice as a rsult of the different sizes of the solute and solvent atoms, would be partially relieved. Later, Nowick (1952) and Leclaire and Lomer (1954) have postulated more elaborate geometrical schemes for the process. They have, however, retained Zener's idea that the effect arises fundamentally from a microscopic rearrangement of atoms when the material is placed under stress, i.e. stress-induced short range ordering. The latter workers presume that the relaxation arises from lattice dilatation accompanying changes in the degree of order and express the damping of a given alloy in terms of a number of parameters including the short range order parameter, σ. The effect of the degree of order on damping has been verified by Lulay and Wert (1956) in MgCd alloys.

In the present paper an account is given of the investigations of the anelastic effects in α-AgCd alloys. This was chosen since the diffusion data for it are available through the measurement of tracer diffusion by Manning (1959) and these could be utilized to compare and interprete the results of the anelastic measurements. Internal frictions in 30.8% α-brass was also measured in order to compare the efficiency of the torsion pendulum constructed by the author.

THEORY AND FORMULAE

Nowick (1952) made the assumption that since the essential atomic process involved in a change in order, which is responsible for the relaxation of strain when a stress is applied to the solid, is the replacement, on a number of lattice sites, of one type of atom by another, then the relaxation rate $1/\tau$ should be simply proportional to Γ_r, the mean rate at which a replacement on a given site occurs. Thus

$$1/\tau = \alpha\Gamma_r \qquad \ldots (1)$$

and

$$D = \beta a^2\Gamma_r \qquad \ldots (2)$$

where D is the diffusion coefficient of the alloy in the absence of concentration gradients, 'a' is the lattice parameter and β is a geometrical factor and is 1/12 for f.c.c. lattice. The dimentionless proportionality constant α is of the order of unity. The relaxation time τ obeys the Arrhenius type equation

$$\tau = \tau_0 e^{H/RT} \qquad \ldots (3)$$

where H is the activation energy, R the gas constant and T the absolute temperature.

For the standard linear solids in the sense defined by Zener (1948), strain is not simply proportional to the stress but the two quantities are also connected with their first time derivatives by means of a linear relation which, for a vibrating solid, leads to an expression for the internal friction, Q^{-1} in terms of the angular frequency of oscillation ω and a mean relaxation time τ.

$$Q^{-1} = \Delta_M \frac{\omega\tau}{1+(\omega\tau)^2} \quad \ldots \quad (4)$$

where Δ_M 'the relaxation strength' is a measure of the magnitude of the effect. Eq.(4) gives the well known internal friction peak with maximum value of $\omega\tau = 1$. Thus if T_m is the temperature of maximum damping, we have

$$\tau_{Tm} = \frac{1}{\omega} \quad \ldots \quad (5)$$

as the basis for the determination of τ at one particular temperature T_m from an internal friction peak.

EXPERIMENTAL MEASUREMENT OF INTERNAL FRICTION

The internal friction measurements were carried out in a torsional pendulum which is patterned after *Kê*(1947) and is shown diagrammatically in Fig. 1. The wire specimen *S* is firmly clamped between the upper V-grip *V* and the lower pinvise *p*. The pinvice is welded to a thick nichrome wire (B and S gauge No. 13) which is a poor conductor of heat but has a much higher rigidity than the test wire at various higher temperatures. A galvanometer mirror *M* mounted on the nichrome wire reflects the image of a straight filament on to the photographic recorder two meters away. BB is a torsional bar about 8″ inches long carrying at each end a small iron weight. The torsional vibration can be set up by momentarily actuating two small electromagnets placed at a suitable distance from the iron weights and the vibrations are recorded photographically on a rotating drum. The pendulum is heated in an electrically heated tube furnace and the temperature is recorded by a calibrated chromel-alumel thermocouple placed close to the specimen.

α-AgCd alloys with 33.8, 29.3 and 24.3 at. % Cd and α-brass with 30.8 at. % Zn were prepared by melting appropriate quantities of the spectroscopically pure metals as described earlier (Quader, 1960). The alloys thus prepared were taken in evacuated Pyrex tubes and homogenized at 650°C for two days, then reduced in diameter by rolling and finally drawn down to wire of 1 mm diameter for use in the torsional pendulum. The wires were cut to proper size (7″ long), straightened and again sealed in evacuated Pyrex tubes and annealed at 600°C for 6 hours and thereby developed uniform grains with the average grain size of .02 cm.

The AgCd specimen was mounted in the pendulum and annealed there for 15 mins. at about 430°C, and internal friction measurements were obtained during cooling and subsequent heating of the pendulum. The maximum ampli-

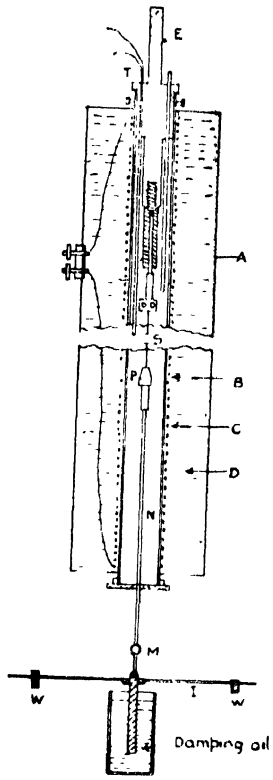

Fig. 1. Torsional pendulum.

tude of oscillation in all the measurements was not allowed to exceed that corresponding to a torsional strain of 4×10^{-5}. For this small strain the decrement was found to be independent of the amplitude. At the ends of the measurements the wires were examined by taking X-ray diffraction photographs to ensure that no appreciable loss of Cd had occurred during measurements. The α-brass specimen was annealed at 530°C for one hour after mounting in the pendulum and measurements were taken both during cooling and heating of the pendulum.

The internal friction and rigidity were obtained by measuring respectively the logarithmic decrement and the frequency of the free torsional vibration of the pendulum. The measure of internal friction (Q^{-1}) herein adopted was the logarithmic decrement divided by π.

EXPERIMENTAL RESULTS

(a) *AgCd Measurements* :

Typical internal friction curves for the three α-AgCd alloys, measured at two different frequencies of vibrations, are shown in Fig. 2 and have been plotted as

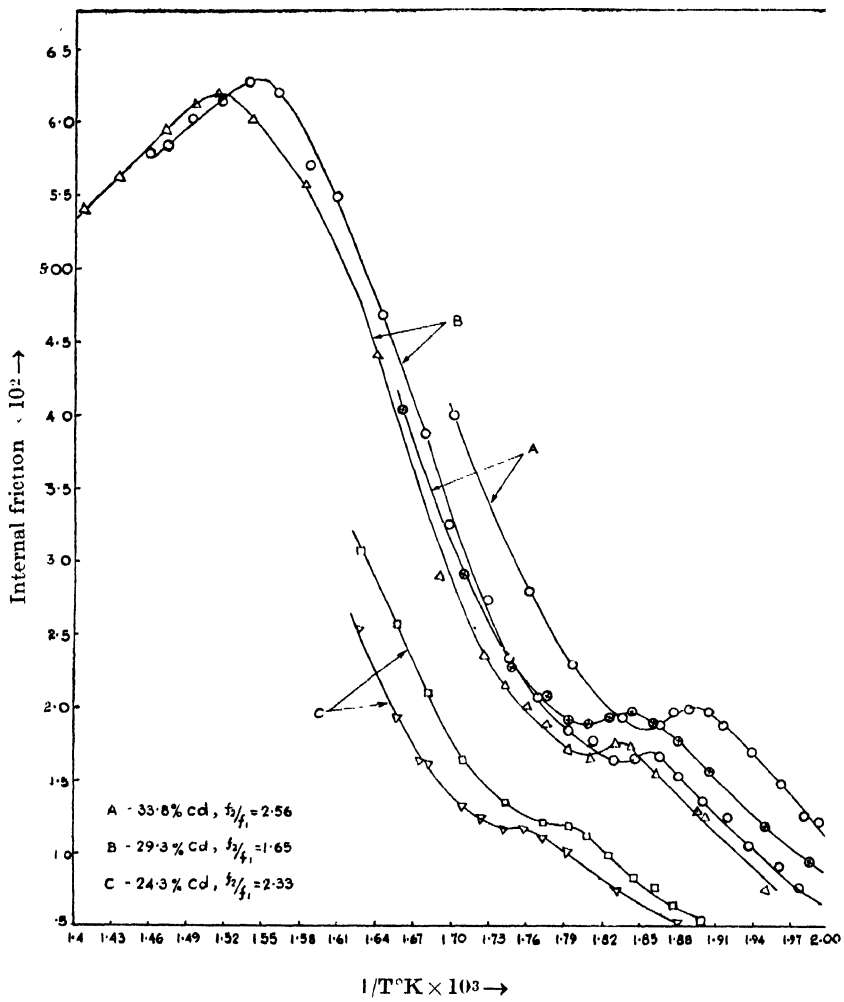

Fig. 2. Internal friction, inverse temperature for α-Ag-Cd alloys.

a function of reciprocal of the absolute temperature. In these curves a small peak occurs (such as one at 266°C at 0.88 c/s for the 29.3 % alloy) followed by a broader grain boundary peak at a higher temperature. The weak internal friction peak is due to the relaxation effects similar to that observed by Zener (1943) and Kê (1948) in 30% α-brass and is due to stress induced ordering in the alloy.

From the curves it is evident that the peak height increases with increasing Cd content and varies roughly as the square of the Cd-concentration. Since the grain boundary relaxation greatly affects the height of the order peak, a correct estimation of the relaxation strength which is twice the height of the peak is not possible. However, the location of the peak, which, according to Nowick (1952), is unaffected by the grain size, can be obtained from the graph within ± 1°C. Hence from the frequency and the temperature at the maximum, the corresponding relaxation time can be obtained from Eq.(5). The activation energy H is obtained from the shift of the maximum with the frequency with the help of the relation.

$$H = R \ln(f_2/f_1) \Big/ \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad \ldots \quad (6)$$

where the two frequencims f_1 and f_2 correspond to the temperatures T_1 and T_2. The results are given in Table I.

TABLE I

Activation energy for the Zener and grain boundary relaxations

Alloy system	Composition at. % solute	H_{order} in K cal/mole	H_{gb} in K cal/mole
Ag-Cd	24.3	39.36	
	29.3	38.77	39.1
	33.8	38.45	
Cu-Zn	30.8	39.17	39.84

The activation energy is found to decrease with increase of cadmium concentration in a linear fashion. Hence, by extrapolating the straight line plot of the activation energy against Cd concentration to 0 % Cd we get $H_{0\%Cd} = 41.6$K cal/mole which is close to the value 41.7K cal/mole for tracer diffusion of Cd in pure silver (Tomizuka *et al.*, 1954). However, in case of AgZn alloy Nowick got $H_{0\%Zn} = 40.6$K cal which he assumed to correspond to the activation energy of self diffusion of silver.

The internal friction maximum due to grain boundary relaxation was measured only in 29.3% Cd alloy, and the corresponding activation energy $H_{gb} = 39.17$ K cal/mole was obtained. According to Pearson (1956), $H_{gb} = 38.00$K cal/mole for 1.e 32.4% Cd alloy. The mechanism of grain boundary relaxation is not clearly

known, but various observations show that it is probably connected with the movements of dislocation in grain boundary.

(b) *CuZn Measurement* :

The internal friction in 30.8 at % Zn α-brass was measured at three different frequencies and the results are shown in Fig. 3. The curves are similar to those

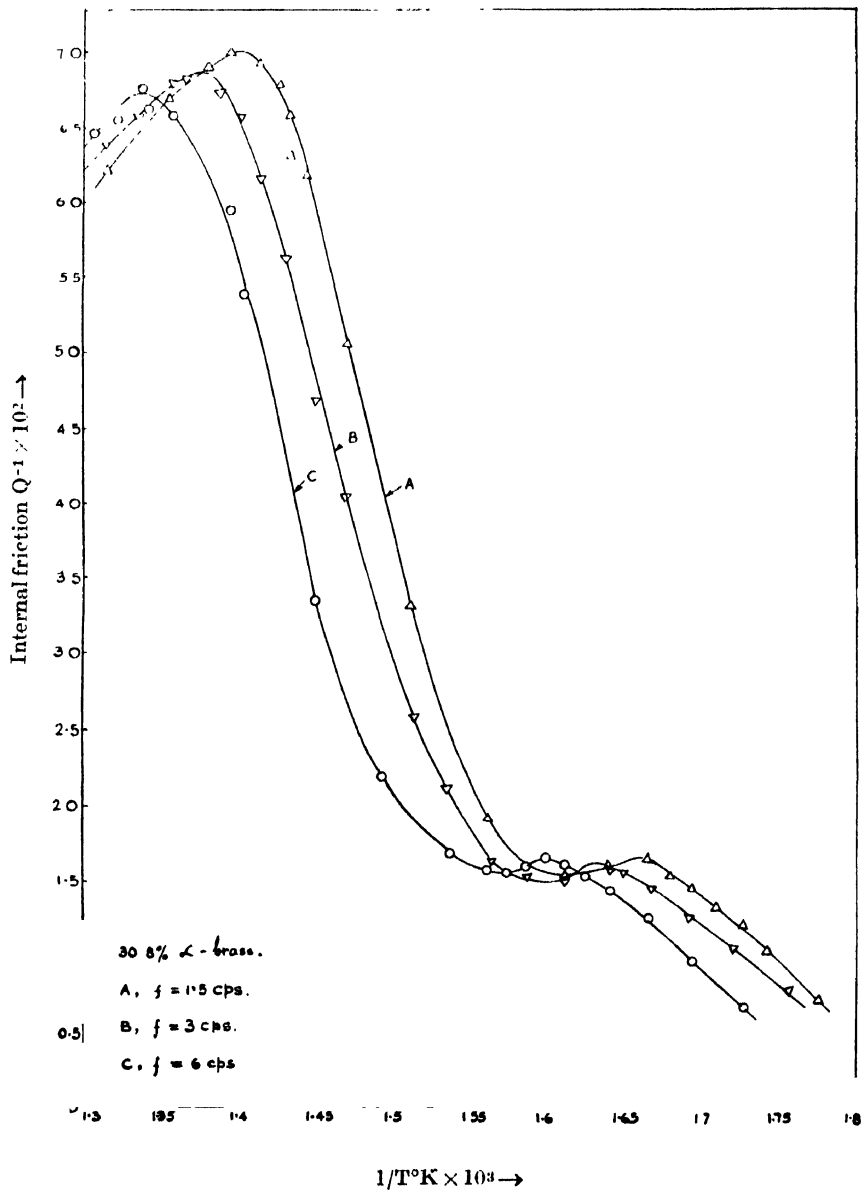

Fig. 3. Internal friction, inverse temperature for 30.8% α-brass.

obtained by Kê (1948) for polycrystalline 29 at.% α-brass. The activation energy was calculated from the shift of the peaks and H_{order} — 39.17Kcal/mole and H_{gb} = 39.84Kcal/mole are obtained for the Zener and grain boundary relaxations respectively. According to Kê the corresponding values are H_{order} =41.7K cal/mole and H_{gb} = 41.00Kcal/mole for the 29 at. % brass whereas Leclaire (1954) in a precision measurement with single crystal wire specimen got H_{order} = 37.3 ± 1 Kcal/mole. The latter workers put forward a new theory of relaxation strength based on the assumption of lattice dilatation accompanying changes in the order and obtained satisfactory agreement between the theoretically calculated and experimentally measured relaxation strength in a series of α - CuZn alloys.

c) *Measurement of rigidity modulus* :

The frequency of vibration of the pendulum was measured at different temperatures along with the internal friction measurements. Since the rigidity modulus G of the wire is proportional to the square of the frequency of vibration when the internal friction is small, some additional information may be obtained from a plot of frequency squared against temperature. Such curves for the 29.3% AgCd and 30.8% CuZn alloys are shown in Fig. 4. The curves are similar to

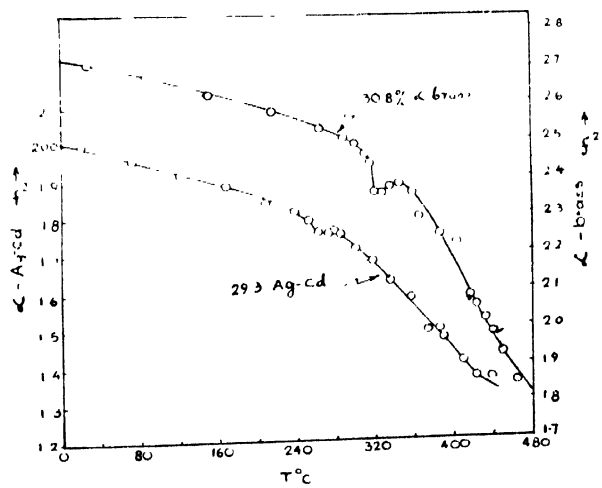

Fig. 4. f^2 -T for 29.3% AgCd and 30.8% CuZn alloys.

that obtained by Kê (1948) for α-brass and represent the variation of rigidity with temperature. The deviation of the rigidity from linearity at higher tem-

peratures, say, above 200°C for the 29.3% alloy, is due to the grain boundary relaxation effects. The small dip at 266° corresponds to the internal friction peak due to ordering. Similar is the case with α-brass when the dip occurs at 328°C corresponding to the order peak.

DISCUSSION

If the relaxation effects are to be ascribed to the local atomic rearrangement produced under stress, then the relaxation time τ should be of the order of the atomic jump rate $a^2/12D$, where D is the diffusion coefficient in the absence of a concentration gradient. That this is so has been shown experimentally by Leclaire (1954) for a no. of alloys where both the diffusion and relaxation data are available. A similar comparison between the relaxation times and the diffusion coefficients is shown in Fig. 5 for the Ag-Cd alloys in which log D and log $a^2/12\tau$ values are

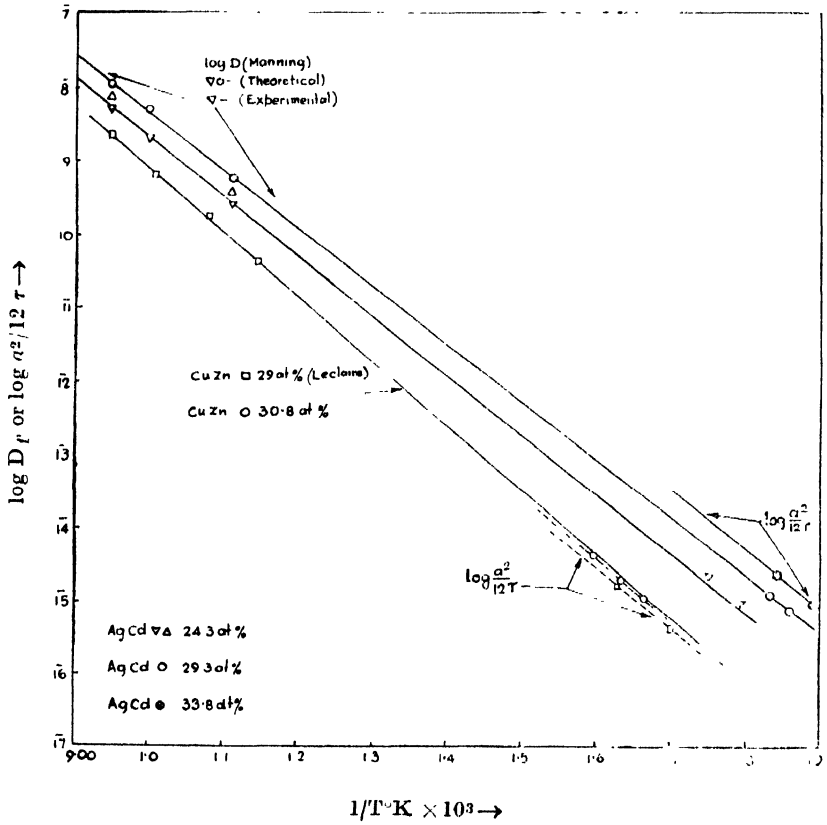

Fig. 5. Comparison of diffusion coefficient and $a^2/12\tau$ values.

plotted against inverse absolute temperature. The approximate values of chemical diffusion coefficients, D_{chem} for the 24.3 and 29.3% Cd alloys at three different

temperatures were obtained from Manning's (1959) curves, who measured the tracer diffusion in AgCd alloys up to 27 at.% Cd. He also calculated D_{chem} from the Darkens' (1948) theoretical relation,

$$D_{chem} = (f_{Ag}D_{Cd} + f_{Cd}D_{Ag})\left(1 + \frac{d(\ln\gamma_i)}{d(\ln f_i)}\right) \quad \ldots (7)$$

using Schoen's tracer diffusion values D_i and the thermodynamic factor from Herasymenko's (1956) vapour pressure data. The experimental D_{chem} values are usually higher than the calculated ones, and are, according to Manning, probably somewhat in error at the limiting concentrations. The D_{chem} values for the 29.3% alloy were, therefore, obtained by extrapolating the theoretical curves only. However, for the 24.3% alloy both the theoretically calculated and experimental values of D_{chem} were read out directly from his curves. The D_{chem} values were corrected for the thermodynamic factor, also obtained from Manning, before use for comparison with the anelastic data. The value of D so obtained are given in Table II. The log $a^2/12\tau$ values for all the alloys are recorded in Table III.

TABLE II

Directly measured diffusion coefficients of AgCd alloys as obtained from Manning (1959)

Composition at. % Cd.	$1+\frac{d(ln\gamma_i)}{d(lnf_i)}$	T K	1/T K 10^3	log D calculated from theoretical curve	log D calculated from experimental curve
		900	1.111	$\bar{10}.394$	$\bar{10}.530$
24.3	2.5	1000	1.000	9.309	9.309
		1053	0.949	9.716	9.852
		900	1.111	$\bar{10}.753$	
29.3	3.0	1000	1.000	$\bar{9}.602$	
		1053	0.949	8.025	

For the sake of comparison the log $a^2/12\tau$ values for 30.8% α-brass are also shown in Fig. 5 along with the diffusion and anelastic data for the 29% α-brass taken from Leclaire (1951). For the 30.8% brass the log $a^2/12\tau$ vlaes are higher than those of 29% brass and are, as expected, giving a higher value for the diffusion coefficient.

TABLE III

Diffusion coefficient calculated from anelastic measurements

Alloy system	Composition at.% solute	T°K	1/T°K × 10³	log $a^2/12\tau$
	24.3	558	1.793	16.965
	-	572	1.750	15.333
	29.3	538.5	1.858	16.858
Ag-Cd	- -	546	1.832	15.077
	33.8	529	1.891	16.940
	—	543	1.842	15.349
		601	1.664	15.038
Cu-Zn	30.8	612	1 633	15.283
		626	1.597	15.603

It is evident from Fig. 5 that for AgCd alloys the log $a^2/12\tau$ values are, within the limits of the experimental error, either slightly above or in the same line with the log D values obtained from Manning's theoretical curves. But when the experimental values of D_{chem} were considered the anelastic data fall below the extrapolated log D, and this for the 24.3% alloy is shown in Fig. 5. These results are in agreement with the observations of Laclaire (1954) in other alloys supporting Nowick's conclusion that τ, unlike D, is governed mainly by the diffusion rate of the more slowly moving components. Based on the above assumption Nowick gave an approximate relation for Γ_τ, the mean rate of replacement

$$\frac{1}{\Gamma_\tau} \simeq \frac{a^2}{24}\left(\frac{1}{f_A D_A} \quad \frac{1}{f_B D_B}\right) \qquad \ldots \quad (8)$$

connecting D_A and D_B, the atom self-diffusion coefficients. Leclaire (1954) in a critical discussion argued that the Eq. (8) should not hold for extreme compositions where the atoms of one type are, for the most part, distributed singly in a matrix of the other. Movements of such isolated atoms, if sufficiently far apart, would not affect the order or give rise to a relaxation of stress or strain and the effects observed would correspond to rearrangements involving groups of two or more solute atoms. The Γ_τ approrpiate to the extreme concentrations will be more nearly the mean Γ_τ of an intermediate concentration.

Nowick made an estimate of α(see, Eq. 1) by assuming for τ_0 an expression similar to that derived by Zener (1948) for the case of D_0 in self-diffusion and comparing with the value of τ_0 obtained experimentally. Thus he obtained $\alpha \simeq 0.3$ for the AgZn alloys. For the 30% α-brass Leclaire calculated Eq.(8) in terms of D_{Zn} and D_{Zn}/D and compared the measured (τ) and calculated ($\alpha\tau$) values. In this calculation he used a constant value of 1.26 for D_{Zn}/D for all the temperatures. From the observation he concluded that at least for 30%α-brass Nowick's relation seems to be valid with α closely equal to unity.

Nowick's expression was recalculated for the AgCd alloys in terms of D ($D = f_A D_B + f_B D_A$) and D_{Cd}/D_{Ag} values of Manning's tracer diffusion measurements. The logarithm of the calculated ($\alpha\tau$) and measured (τ) values are plotted against $1/T$ in Fig. 6. Reference to the figure shows that the $\alpha\tau$ and τ values do

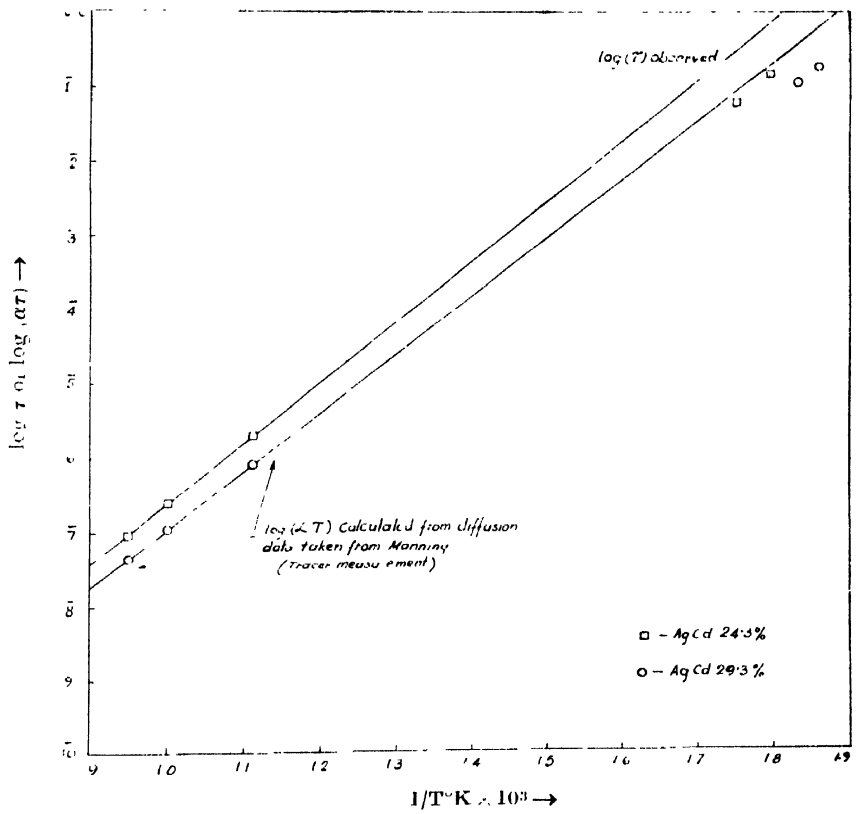

Fig. 6. Comparison of log ($\alpha\tau$) calculated and log (τ) observed for 24.3 and 29.3% AgCd alloys.

not fall on the same line, the former being higher, showing that the α is greater than unity. To make the calculated τ values fall on the same line with the measured ones, α should be equal to 2.8 and 3.1 respectively for the 29.3 and 24.3% alloys. This result that α is higher than unity seems unreasonable, since

it means that the relaxation frequency is somewhat more than the rate controlling jump frequency. Thus it would appear that either Nowick's relation does not hold for the AgCd α-phase alloys or the diffusion data are somewhat in error. Clearly therefore, additional data for τ in the case of these alloys are required at temperatures close to those of the diffusion measurements so as to avoid the uncertainties introduced by extrapolation.

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